PHYSICO-CHEMICAL STUDIES OF FORMATION OF COORDINATION COMPOUNDS OF SOME TRANSITION METALS WITH BIOLOGICALLY ACTIVE SCHIFF'S BASE LIGANDS

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Abstract: I study the pH metric titration of complexes of bivalent transition metals cobalt, nickel, copper, zinc and cadmium with valine ligand.

Most commonly employed technique for determination of stability constants of coordination compounds are potentiometric method, polarography, photometric method, stability method and liquid-liquid partition method.

The idea of the stability constant of a coordination compound have their unit in evaluating its potential for biological and catalytic activity. It will be also very useful in drug discovery and designing of new drugs.

***Index terms*: Bivalent Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) transition metals with valine ligand, Bjerrum's pH-metric titration technique modified by Irving and Rossotti, proton-ligand stability constant.**

I. INTRODUCTION

These days chemistry of coordination compounds of transition metals has drawn considerable attention of the inorganic and organic fields. Complex compounds have different individual applications [1-4].

A large number of Schiff's base and their metal complexes with transition metals have been reported in literature [5-10]. Schiff's base complexes play an important role in the biological process [11-22]. It has been established that biological activity of a ligand is enhanced many fold on its co-ordination with suitable metal ions. Coordination compounds have applications in the field of medicines, insecticides, colour pigments and dyes.

II. MATERIALS AND METHODS

2.1. Materials

(a) Bivalent metal salts of transition metals cobalt, nickel, copper, zinc and cadmium with valine ligand.

2.2. Method

Bjerrum's pH metric titration technique modified by Irving and Rossotti will be performed for the determination of protonation constant.

pH metric titrations were done at constant ionic strength of 0.10 (M) KNO_3 at two different temperatures 293K and 303K within the limit of ±1K.

Titrations were carried out in a small long neck beaker called cell. The cell stirrer, micro burette and electrodes of the pH-meter were kept in the thermo stat for two hours to attain the specified temperature. Then pure nitrogen gas was passed through the inlet for 20 minutes and solution was mixed with the stirrer. Every time equilibrium attained quickly. In every case titration were performed in duplicate to verify the results.

III. RESULTS AND DISCUSSION

3.1. pH metric titration with valine ligand

Calvin-Bjerrum pH metric titration of ligand valine with metal ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) at two temperatures 293K and 303K were carried out.

The following set of mixtures were prepared for titration.

1. 1.0 mL (0.1M) HNO_3 + 10.0 mL (1.0M) KNO_3 + 39.0 mL water + 50.0 mL ethanol.
2. 1.0 mL (0.1M) HNO_3 + 5.0 mL (1.0M) KNO_3 + 15.0 mL (M/20) ligand + 39.0 mL water + 40.0 mL ethanol.
3. 1.0 mL (0.1M) HNO_3 + 15.0 mL (1.0M) KNO_3 + 1.0 mL (M/20) metal solution + 5.0 mL (M/20) ligand + 30.0 mL water + 48.0mL ethanol

Total volume V^0 in each set was 100.0 mL and water-ethanol ratio was 1:1 (v/v).

3.1.1. Titration of the acid

Mixture number 1 as mentioned above was taken in the titration cell and when it attained a constant temperature, it was titrated against standard alkali solution (1.0 M). The change in pH of the solution with each addition of alkali was recorded. It was mentioned in table no. 1.1 at temperature 293K and table no. 1.2 at 303K respectively.

3.1.2. Titration of the Acid + Ligand

Mixture number 2 as mentioned above was taken in a clean titrating beaker, when it attained the same constant temperature it was titrated as above. The change in pH with addition of alkali was recorded as in table no. 1.1 at temperature 293K and table no. 1.2 at temperature 303K.

3.1.3. Titration of the mixture of acid, ligand and metal ions

Mixture number 3 as mentioned above was taken in titrating beaker and when it attained the same constant temperature, it was titrated as above.

Change in pH with each addition of alkali was recorded as mentioned in table no. 1.1 at temperature 293K and table no. 1.2 at temperature 303K.The same process were repeated for five different metals.

The metal ions selected for this project were Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

During the titrations, the change in colour and appearance of turbidity at particular pH were recorded simultaneously.

A graph between pH-meter reading [B] and volume of alkali added were plotted in each case. The titration curves so obtained for each metal ion are referred as:

(a) Acid titration curve

(b) Ligand titration curve and

(c) Complex titration curves respectively.

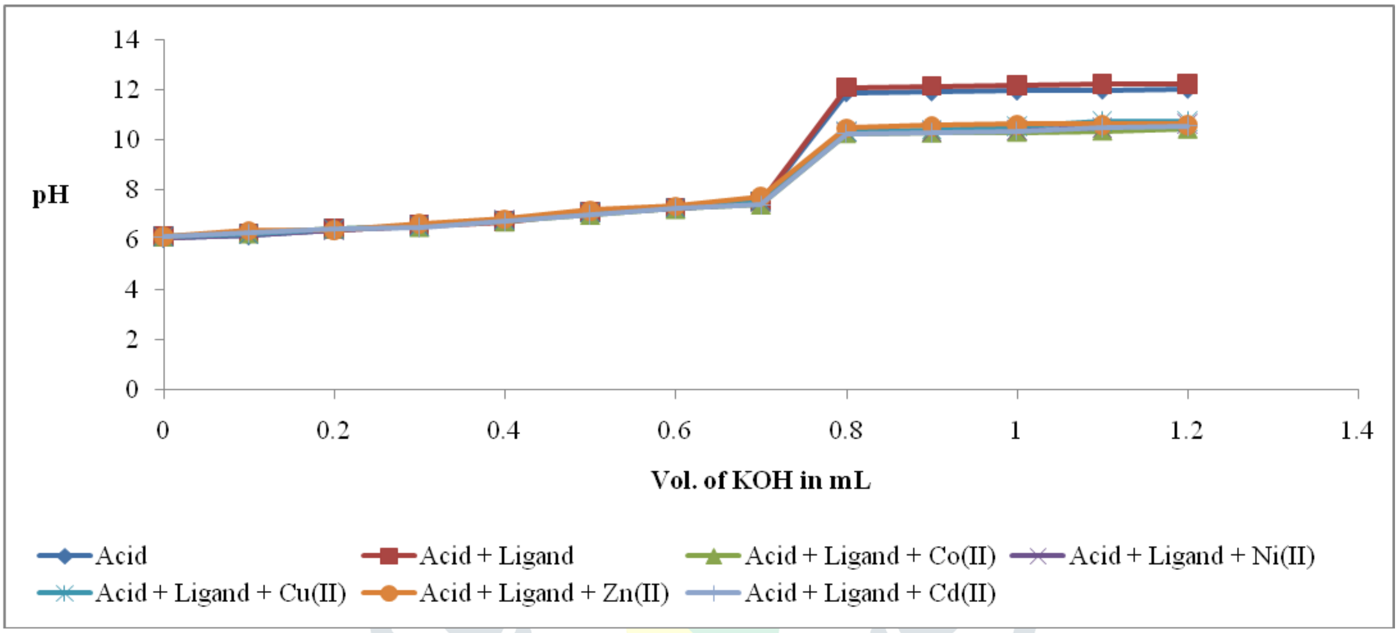
Table 1.1. Results of three titration (i) Acid (ii) Acid + Ligand (iii) Acid + Ligand + Metal ions.

Ligand - Valine Temperature-293±1K μ^0=0.1(M) KNO_3

Water-Ethanol ratio=1:1 (v/v)

Vol. of alkali added in mL	pH						
	Acid	Acid + Ligand	Acid + Ligand + Co(II)	Acid + Ligand + Ni(II)	Acid + Ligand + Cu(II)	Acid + Ligand + Zn(II)	Acid + Ligand + Cd(II)
0.00	6.10	6.11	6.14	6.11	6.12	6.14	6.15
0.10	6.20	6.24	6.28	6.19	6.24	6.39	6.29
0.20	6.40	6.43	6.46	6.39	6.43	6.40	6.46
0.30	6.60	6.59	6.53	6.57	6.55	6.67	6.51
0.40	6.80	6.73	6.75	6.82	6.77	6.85	6.75

0.50	7.10	7.11	7.01	7.09	7.11	7.19	7.02
0.60	7.30	7.29	7.25	7.27	7.29	7.37	7.29
0.70	7.50	7.54	7.42	7.49	7.55	7.73	7.41
0.80	11.90	12.12	10.27	10.29	10.33	10.49	10.26
0.90	11.94	12.17	10.29	10.31	10.41	10.56	10.28
1.00	11.97	12.19	10.32	10.37	10.54	10.63	10.36
1.10	12.01	12.23	10.37	10.48	10.74	10.61	10.49
1.20	12.04	12.25	10.45	10.64	10.76	10.63	10.55



`**Figure 1.1.** Acid, ligand and complex titration curves

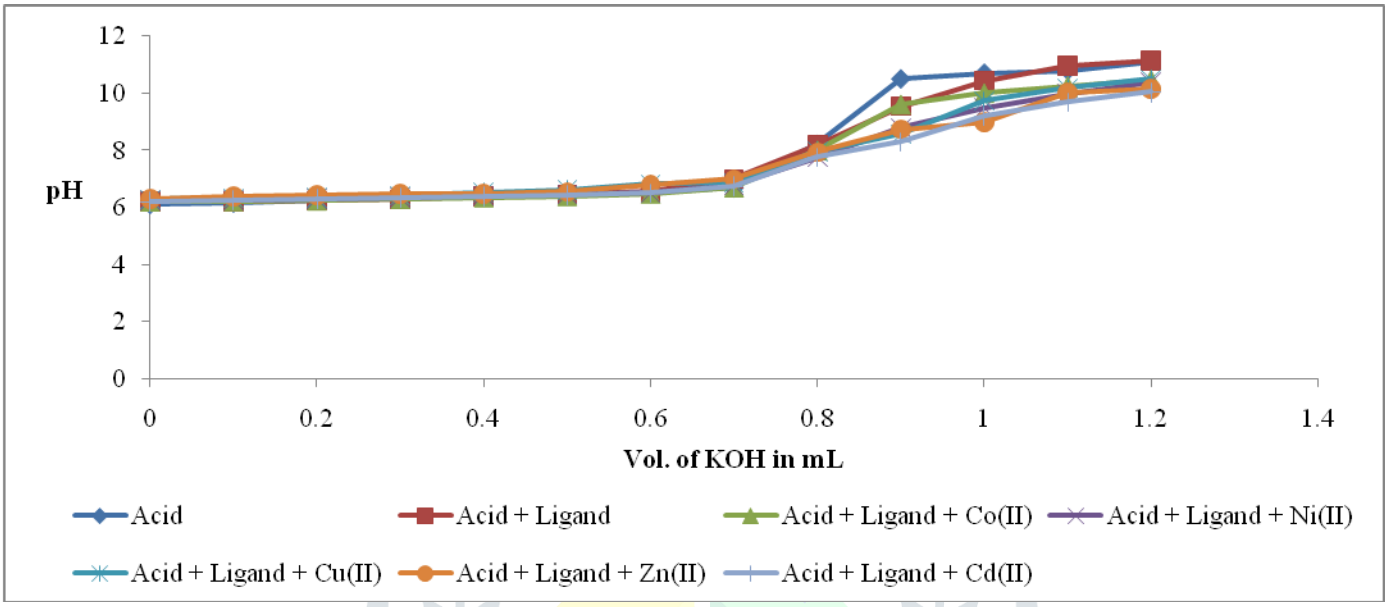
Table 1.2. Results of three titration (i) Acid (ii) Acid + Ligand (iii) Acid + Ligand + Metal ions

Ligand-Valine Temperature-303±1K

μ^0=0.1(M) KNO_3 Water-Ethanol ratio=1:1 (v/v)

Vol. of alkali added in mL	**pH**						
	Acid	**Acid + Ligand**	**Acid + Ligand + Co(II)**	**Acid + Ligand + Ni(II)**	**Acid + Ligand + Cu(II)**	**Acid + Ligand + Zn(II)**	**Acid + Ligand + Cd(II)**
0.00	6.10	6.20	6.20	6.24	6.28	6.30	6.20
0.10	6.15	6.22	6.22	6.25	6.31	6.40	6.25
0.20	6.25	6.23	6.24	6.30	6.34	6.45	6.31
0.30	6.36	6.28	6.30	6.34	6.40	6.48	6.35
0.40	6.40	6.40	6.35	6.41	6.51	6.50	6.40
0.50	6.44	6.46	6.40	6.46	6.60	6.55	6.44

0.60	6.50	6.55	6.48	6.50	6.80	6.80	6.50
0.70	6.68	7.00	6.70	6.80	6.85	7.00	6.75
0.80	8.20	8.20	8.00	7.75	7.95	7.95	7.77
0.90	10.50	9.55	9.60	8.80	8.58	8.75	8.30
1.00	10.70	10.44	10.00	9.50	9.75	9.00	9.20
1.10	10.80	10.95	10.25	10.00	10.20	10.02	9.70
1.20	11.10	11.15	10.47	10.40	10.50	10.17	10.05



`**Figure 1.2.** Acid, ligand and complex titration curves

3.2. Calculation of $\overline{nA}$, $\bar{n}$ and pL

$\overline{nA}$, $\bar{n}$ and pL were calculated using standard expression.

$$\overline{nA} \quad = 1 + \{(V_1 - V_2)(V^0 + V_1)\}\{N^0 + E^0/T_L^0\}$$

$$\bar{n} \quad = \{(V_3 - V_2)/(V^0 + V_1)\}\{(N^0 + E^0)/T_M^0\}(1/\overline{nA})$$

$$pL \quad = \log \left[\sum_{j=0}^{j} P^{H}_{\beta j} \ (1/\text{anti}\log B)\ (V^0 + V_3)/(\,T_L^0 - \bar{n}\,T_M^0)V^0\right]$$

3.3. Proton-Ligand stability constant

The ligand titration curve separates from acid titration curve at pH 12.12 at temperature 293K and at pH 9.60 at temperature 303K. The ligand titration curves run parallel to the acid titration curves indicating the smooth dissociation of ligand.

The value of $\overline{nA}$ at various pH reading [B] were calculated from the acid and ligand titration curves (table no. 2.1 at temperature 293K and table no. 2.2 at temperature 303K).

The formation curves obtained from the plot of $\overline{nA}$ vs [B] (figure no. 2.1.1 at temperature 293K and figure no. 2.2.1 at 303K) show that value of $\overline{nA}$ lies between 0.00 and 1.00. This indicates that ligand is monoprotonic.

Dissociation of ligand may be given as

$$H \rightleftharpoons H^+ + L^-$$

The value of proton ligand stability constant was calculated by half –integral method and it was further corroborated by linear plot method. (log $\overline{nA}$)/(1-$\overline{nA}$) vs [B] (figure no 2.1.2 at temperature 293K and figure no 2.2.2 at temperature 303 K).

Table-2.1

Ligand - Valine Temperature-293±1K

μ^0=0.1(M) KNO_3 Water-Ethanol ratio=1:1 (v/v)

[B]	$V_2 - V_1$	$\overline{nA}$	(log $\overline{nA}$)/(1-$\overline{nA}$)
5.00	0.020	0.79220	0.8156
6.00	0.042	0.75902	0.6796
7.00	0.052	0.73190	0.5672
8.00	0.062	0.69800	0.4267
9.00	0.080	0.66410	0.2862
10.00	0.096	0.63020	0.1457
11.00	0.128	0.59630	0.0052

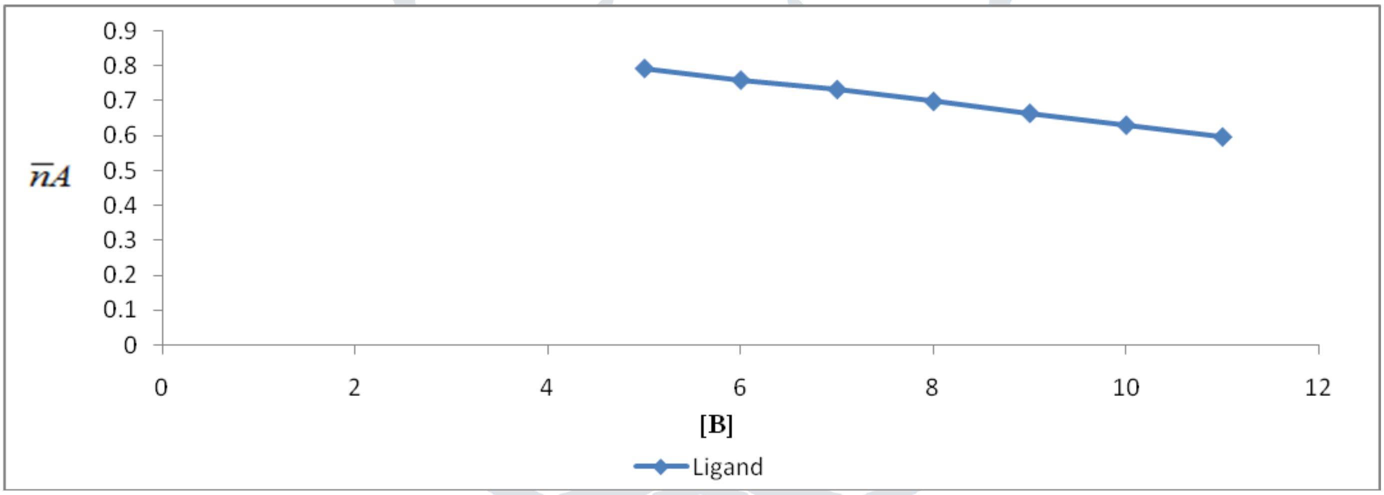


Figure 2.1.1. Formation curve of ligand

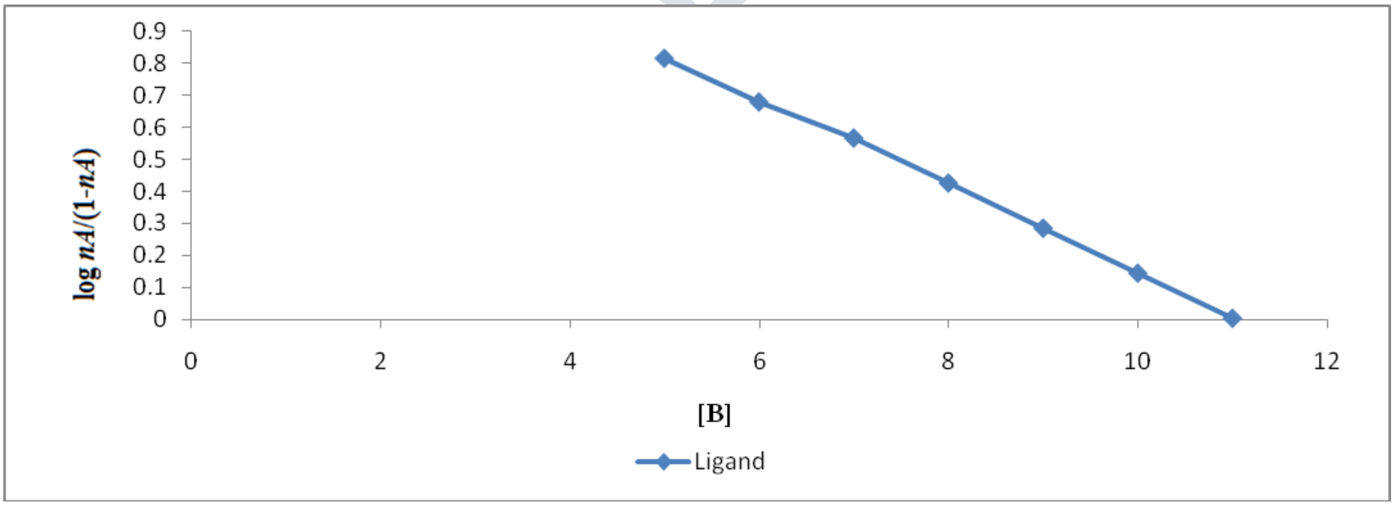


Figure 2.1.2. Linear plot of (log $\overline{nA}$)/(1-$\overline{nA}$) vs [B]

Table-2.2

Ligand-Valine Temperature-303±1K

μ^0=0.1(M) KNO_3 Water-Ethanol ratio=1:1 (v/v)

[B]	$V_2 - V_1$	$\overline{nA}$	(log $\overline{nA}$)/(1-$\overline{nA}$)
5.00	0.026	0.776	0.796
6.00	0.036	0.751	0.673
7.00	0.048	0.722	0.526
8.00	0.066	0.689	0.337
9.00	0.083	0.658	0.219
10.00	0.104	0.627	0.053
11.00	0.128	0.596	-0.142

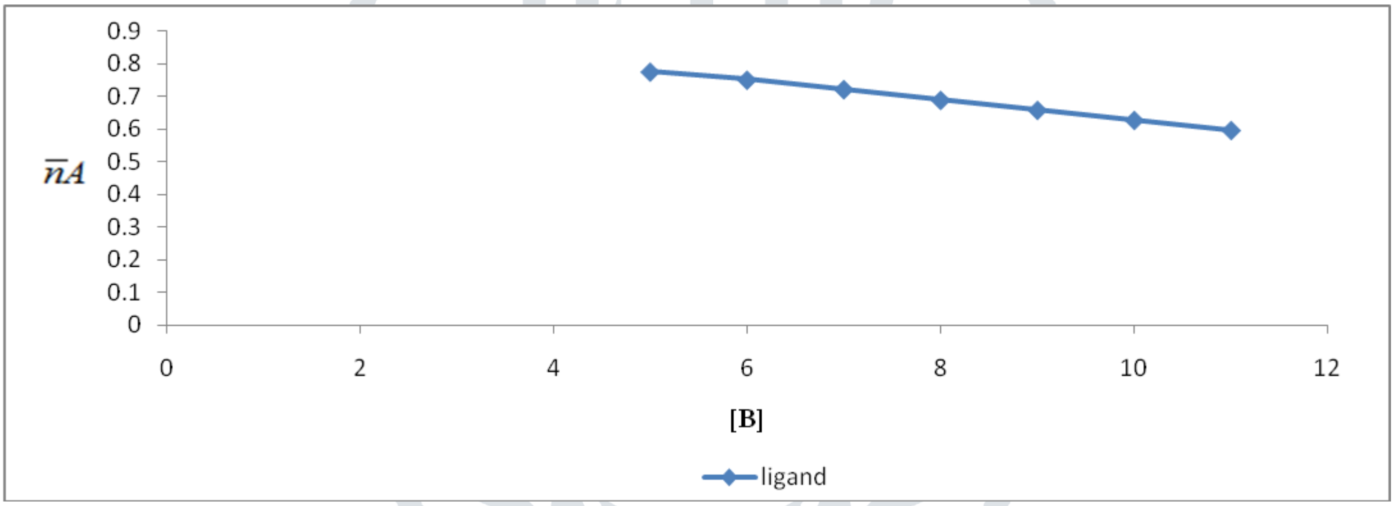


Figure 2.2.1. Formation curves of ligand

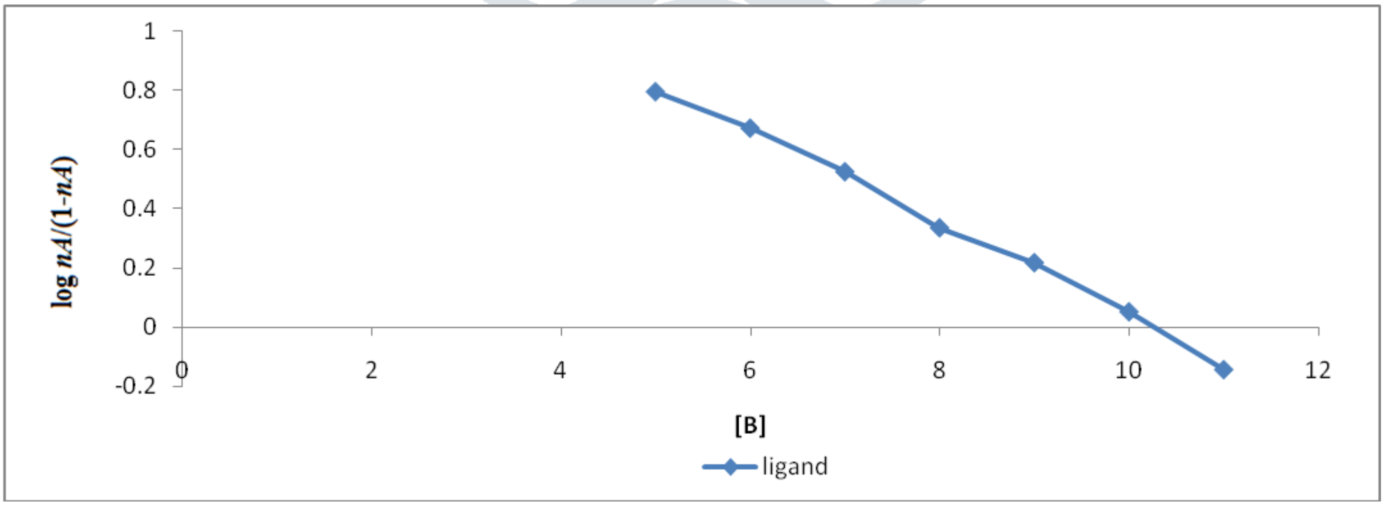


Figure 2.2.2. Linear plot of (log $\overline{nA}$)/(1-$\overline{nA}$) vs [B]

3.4. Metal complexes

3.4.1. Metal complex-Co(II)

Complex titration curves separated from ligand mixture curve at pH=5.2 the curves diverge at pH above.

The value of $\bar{n}$ lies between 0 and 2 (table no. 3.1, figure no. 3.1 at temperature 293K and table no. 3.4, figure no. 3.4 at temperature 303K) indicating the formation of ML and ML_2 types of complexes.

From the formation curves (Figure no. 3.1 and Figure no. 3.4), the values of log K_1 and K_2 were calculated by half-integral method at given two temperatures. The values were corroborated by mid point slope method and linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL (table no. 3.2, figure no. 3.2 at temperature 293K and table no. 3.5, figure no. 3.5 at temperature 303K) and plot of log (2- $\bar{n}$) /($\bar{n}$-1) vs pL (table no. 3.3, figure no. 3.3 at temperature 293K and table no. 3.6, figure no. 3.6 at temperature 303K respectively).

3.4.2. Metal complex-Ni(II)

The complex titration curves crossed the ligand titration curve at pH=5.0 indicating the start of complexation. The curve increased regularly up to pH=8.0 quick but incomplete dissociation of ligand.

No turbidity appears, hence hydrolysis does not take place.

The value of $\bar{n}$ lies between 0 and 2 (table no. 3.1, figure no. 3.1 at temperature 293K and table no. 3.4, figure no. 3.4 at temperature 303K) indicating the formation of ML and ML_2 types of complexes.

From the formation curves (Figure no. 3.1 and Figure no. 3.4), the values of log K_1 and K_2 were calculated by half-integral method at given two temperatures. The values were corroborated by mid point slope method and linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL (table no. 3.2, figure no. 3.2 at temperature 293K and table no. 3.5, figure no. 3.5 at temperature 303K) and plot of log (2- $\bar{n}$) /($\bar{n}$-1) vs pL (table no. 3.3, figure no. 3.3 at temperature 293K and table no. 3.6, figure no. 3.6 at temperature 303K respectively).

3.4.3. Metal complex-Cu(II)

The complex, titration curve separated from ligand mixture curve at pH=7.29 indicating the start of complex formation.

As the metal titration curves did not join up and run parallel to the ligand titration curves indicating liberation of extra proton due to hydrolysis.

Precipitation was observed at pH=7.8. Hence, in order to preclude error due to hydrolysis in the calculation of $\bar{n}$, only the lower pH region of titration curves were used.

The value of $\bar{n}$ lies between 0 and 2 (table no. 3.1, figure no. 3.1 at temperature 293K and table no. 3.4, figure no. 3.4 at temperature 303K) indicating the formation of ML and ML_2 types of complexes.

From the formation curves (Figure no. 3.1 and Figure no. 3.4), the values of log K_1 and K_2 were calculated by half-integral method at given two temperatures. The values were corroborated by mid point slope method and linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL (table no. 3.2, figure no. 3.2 at temperature 293K and table no. 3.5, figure no. 3.5 at temperature 303K) and plot of log (2- $\bar{n}$) /($\bar{n}$-1) vs pL (table no. 3.3, figure no. 3.3 at temperature 293K and table no. 3.6, figure no. 3.6 at temperature 303K respectively).

3.4.4. Metal complex-Zn(II)

The complex curves separated from the ligand titration curves at pH=7.5.

During the titration, no turbidity appears, hence hydrolysis does not take place.

The value of $\bar{n}$ lies between 0 and 2 (table no. 3.1, figure no. 3.1 at temperature 293K and table no. 3.4, figure no. 3.4 at temperature 303K) indicating the formation of ML and ML_2 types of complexes.

From the formation curves (Figure no. 3.1 and Figure no. 3.4), the values of log K_1 and K_2 were calculated by half-integral method at given two temperatures. The values were corroborated by mid point slope method and linear plot of log $\bar{n}$ /(1-

$\bar{n}$) vs pL (table no. 3.2, figure no. 3.2 at temperature 293K and table no. 3.5, figure no. 3.5 at temperature 303K) and plot of log (2- $\bar{n}$) /($\bar{n}$-1) vs pL (table no. 3.3, figure no. 3.3 at temperature 293K and table no. 3.6, figure no. 3.6 at temperature 303K respectively).

3.4.5. Metal complex-Cd(II)

The complex titration curves are separated from the ligand titration curve at pH=7.6. The complex titration curve run parallel to ligand mixture curve up to pH=10.50, then diverged.

During the titration, no turbidity appeared which shoes that hydrolysis does not take place.

The value of $\bar{n}$ lies between 0 and 2 (table no. 3.1, figure no. 3.1 at temperature 293K and table no. 3.4, figure no. 3.4 at temperature 303K) indicating the formation of ML and ML_2 types of complexes.

From the formation curves (Figure no. 3.1 and Figure no. 3.4), the values of log K_1 and K_2 were calculated by half-integral method at given two temperatures. The values were corroborated by mid point slope method and linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL (table no. 3.2, figure no. 3.2 at temperature 293K and table no. 3.5, figure no. 3.5 at temperature 303K) and plot of log (2- $\bar{n}$) /($\bar{n}$-1) vs pL (table no. 3.3, figure no. 3.3 at temperature 293K and table no. 3.6, figure no. 3.6 at temperature 303K respectively).

Table 3.1. Formation curves of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Metal complexes + ligand (valine) Temp: 293K±1K

μ=0.1 (M) KNO_3 Water-Ethanol ratio – 1:1(v/v)

[B]	**pL**	$\bar{n}$				
		Metal complexes				
		Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
5.2	7.409	0.217	0.053	0.035	0.034	0.061
5.4	7.215	0.289	0.986	0.123	0.038	0.204
5.6	7.021	0.364	0.129	0.162	0.138	0.342
5.8	6.827	0.464	0.224	0.152	0.182	0.425
6.0	6.692	0.593	0.354	0.294	0.220	0.460
6.2	6.438	0.726	0.458	0.316	0.325	0.484
6.4	6.244	0.562	0.583	0.564	0.509	0.648
6.6	6.050	1.128	0.762	0.716	0.899	0.843
6.8	5.856	1.104	0.911	0.896	1.035	1.305
7.0	5.661	1.412	1.101	1.283	1.551	1.369
7.2	5.467	1.628	1.297	1.602	1.373	1.680

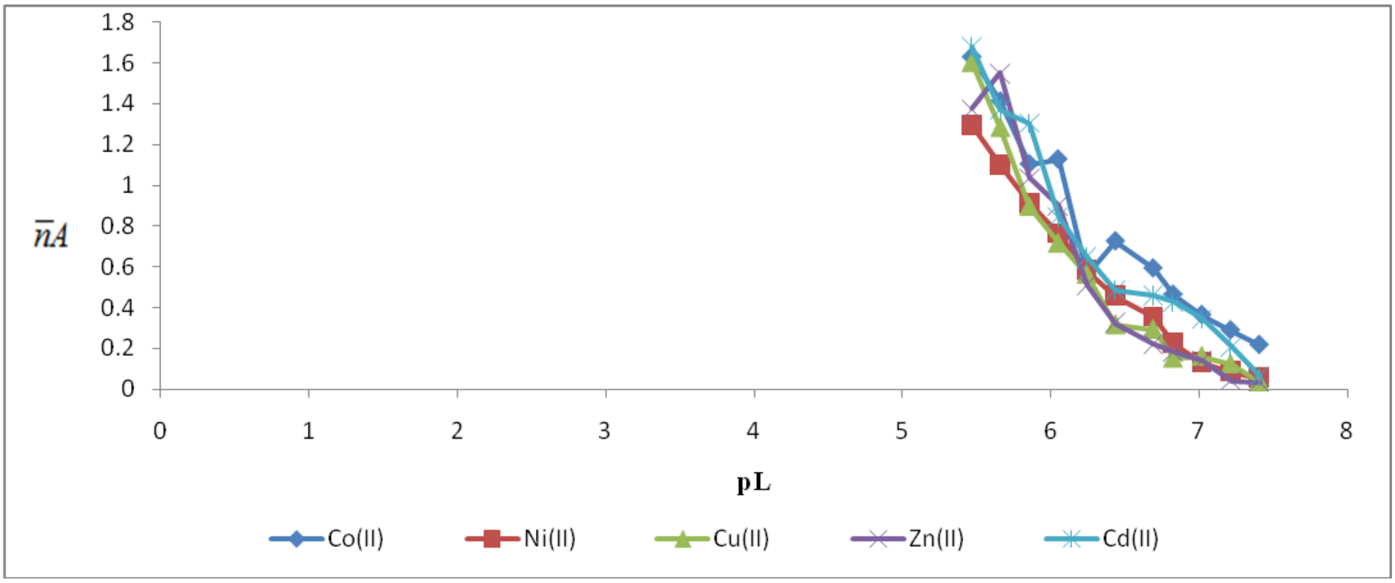


Figure 3.1. Formation curves of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Table 3.2. Linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL

Metal complexes + ligand(valine) Temp: 293K±1K

μ=0.1 (M) KNO$_3$ Water-Ethanol ratio – 1:1(v/v)

pL	**log $\bar{n}$ /(1-$\bar{n}$)**				
		Metal Complexes			
	Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
8.115	-0.976	-0.800	-0.894	-0.594	-0.673
7.922	-0.730	-0.525	-0.652	-0.535	-0.593
7.541	-0.540	-0.318	-0.186	-0.426	-0.377
7.168	-0.341	-0.094	0.296	0.330	0.486
6.983	0.323	0.121	0.648	0.294	0.248

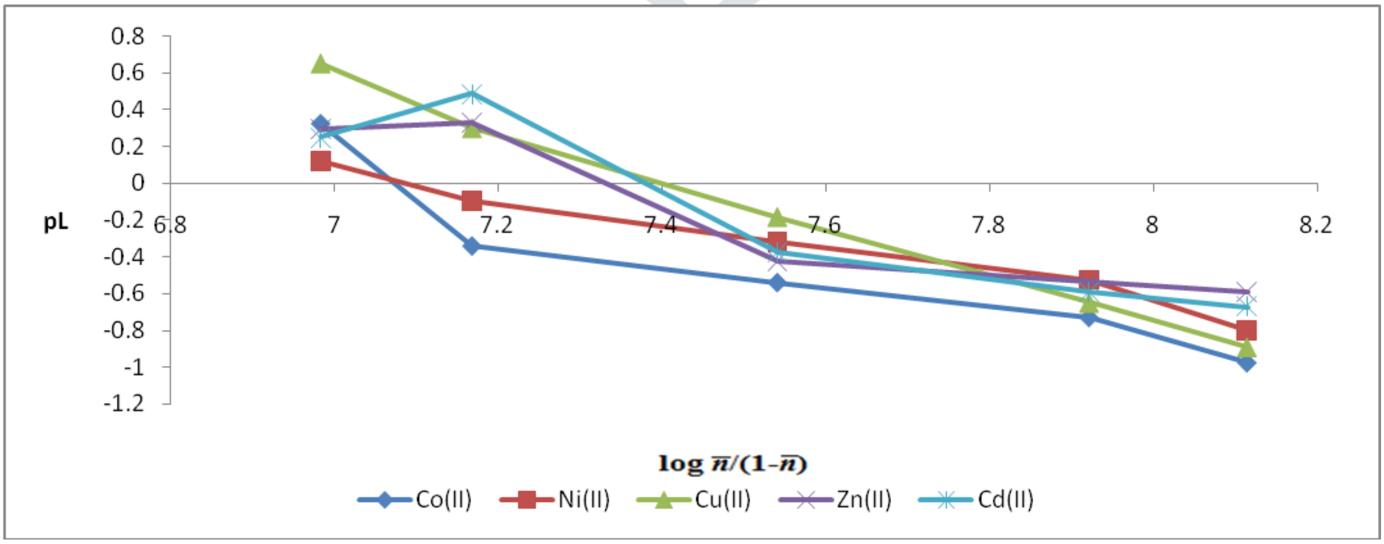


Figure 3.2. Linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL

Table 3.3. Linear plot of log(2- $\bar{n}$) /($\bar{n}$-1) vs pL

Metal complexes + ligand(valine) Temp: 293K±1K

μ=0.1 (M) KNO_3 Water-Ethanol ratio – 1:1(v/v)

pL	**log(2- $\bar{n}$) /($\bar{n}$-1)**				
	Metal Complexes				
	Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
6.623	0.835	0.487	0.647	0.421	0.688
6.449	0.443	0.269	0.172	0.445	0.521
6.277	-0.348	0.182	-0.224	-0.449	-0.650

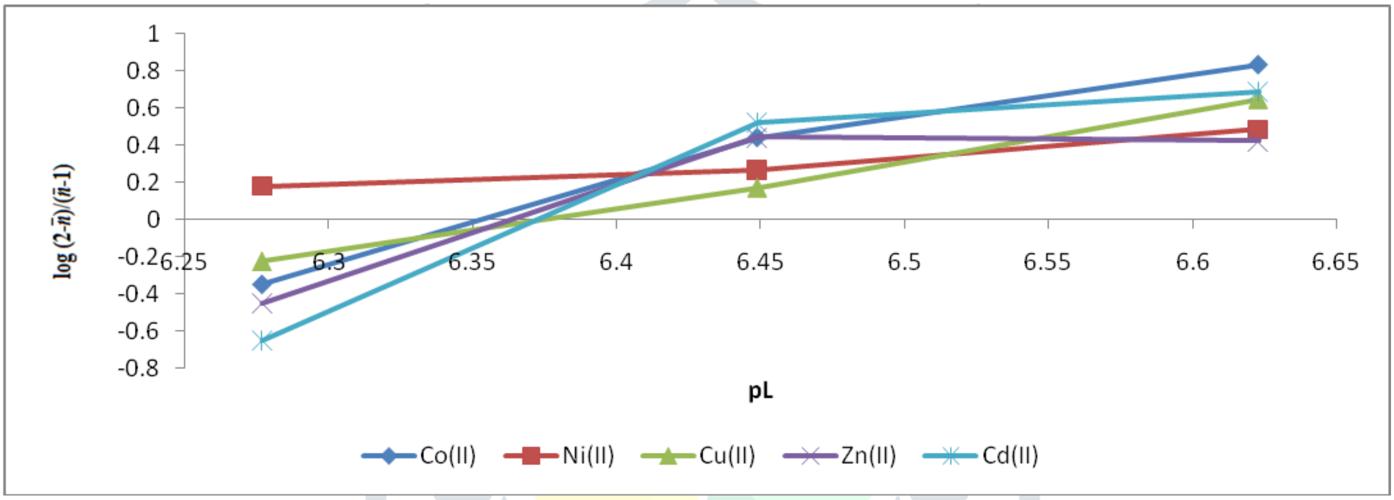


Figure 3.3. Linear plot of log(2- $\bar{n}$) /($\bar{n}$-1) vs pL

Table 3.4. Formation curves of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Metal complexes + ligand(valine) Temp: 303K±1K

μ=0.1 (M) KNO_3 Water-Ethanol ratio – 1:1(v/v)

[B]	**pL**		**$\bar{n}$**			
		Metal complexes				
		Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
5.2	6.314	0.073	0.055	0.035	0.037	0.047
5.4	6.124	0.289	0.237	0.891	0.084	0.096
5.6	5.931	0.388	0.332	0.160	0.244	0.271
5.8	5.740	0.315	0.342	0.331	0.319	0.372
6.0	5.549	0.421	0.393	0.421	0.422	0.504
6.2	5.358	0.532	0.493	0.427	0.555	0.794
6.4	5.166	0.696	0.708	0.541	0.690	0.830

6.6	4.975	0.738	0.754	0.694	0.680	0.832
6.8	4.784	1.245	1.032	0.877	0.885	1.270
7.0	4.592	1.207	1.338	1.241	1.351	1.538
7.2	4.401	1.422	1.563	1.283	1.421	1.662

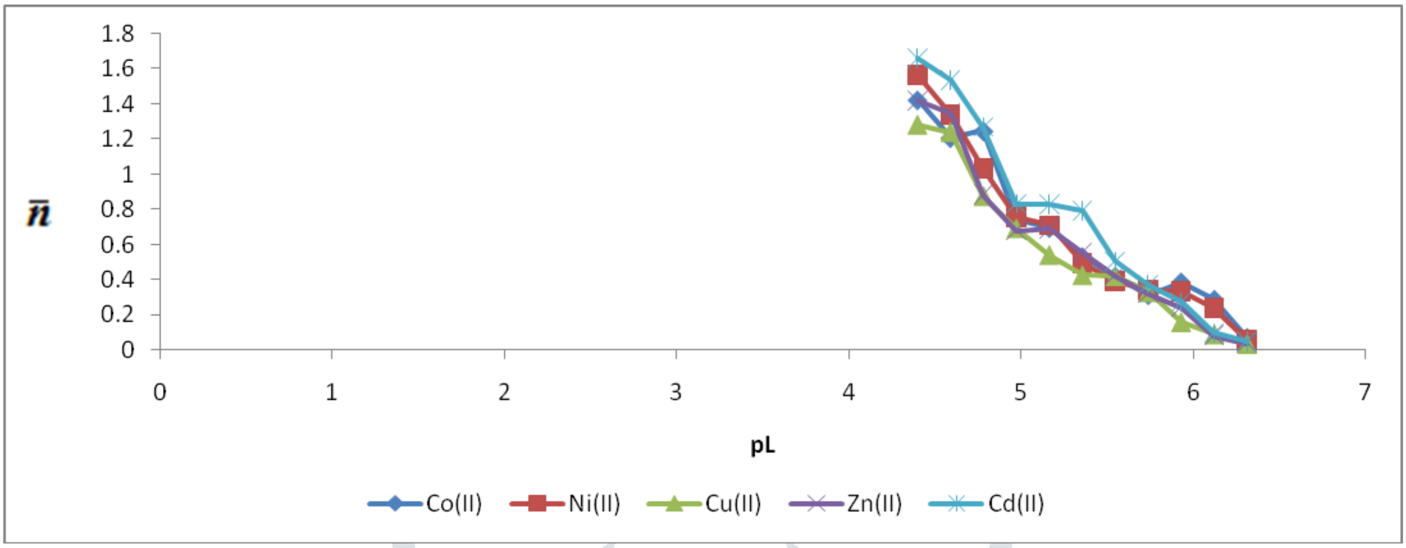


Figure 3.4. Formation curves of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Table 3.5. Linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL

Metal complexes + ligand(valine) Temp: 303K±1K

μ=0.1 (M) KNO_3 Water-Ethanol ratio – 1:1(v/v)

pL	**log $\bar{n}$ /(1-$\bar{n}$)**				
	Metal complexes				
	Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Cd(II)**
6.022	-0.749	-0.602	-0.617	-0.551	-0.585
5.831	-0.691	-0.603	-0.621	-0.322	-0.326
5.641	-0.448	-0.566	-0.422	-0.078	-0.167
5.451	0.335	0.468	0.351	0.158	0.213
5.259	0.291	0.448	0.487	0.555	0.332

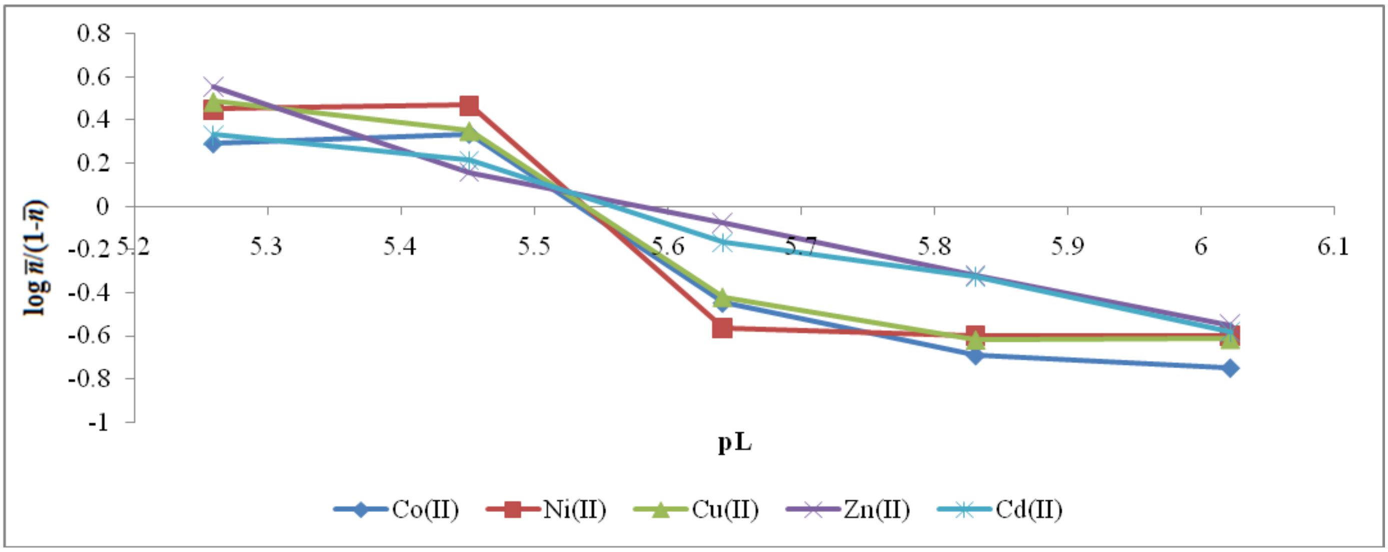


Figure 3.5. Linear plot of log $\bar{n}$ /(1-$\bar{n}$) vs pL

Table 3.6. Linear plot of log(2- $\bar{n}$) /($\bar{n}$-1) vs pL

Metal complexes + ligand(valine) Temp: 303K±1K

μ=0.1 (M) KNO_3 Water-Ethanol ratio – 1:1(v/v)

pL	log(2- $\bar{n}$) /($\bar{n}$-1)				
	Metal Complexes				
	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
5.476	0.869	0.402	0.687	0.572	0.588
5.444	0.297	0.622	0.639	0.337	0.207
5.412	-0.284	0.739	-0.308	-0.553	-0.406
5.381	-0.641	-0.232	-0.421	-0.583	-0.482
5.348	-0.625	-0.325	-0.432	-0.606	-0.402

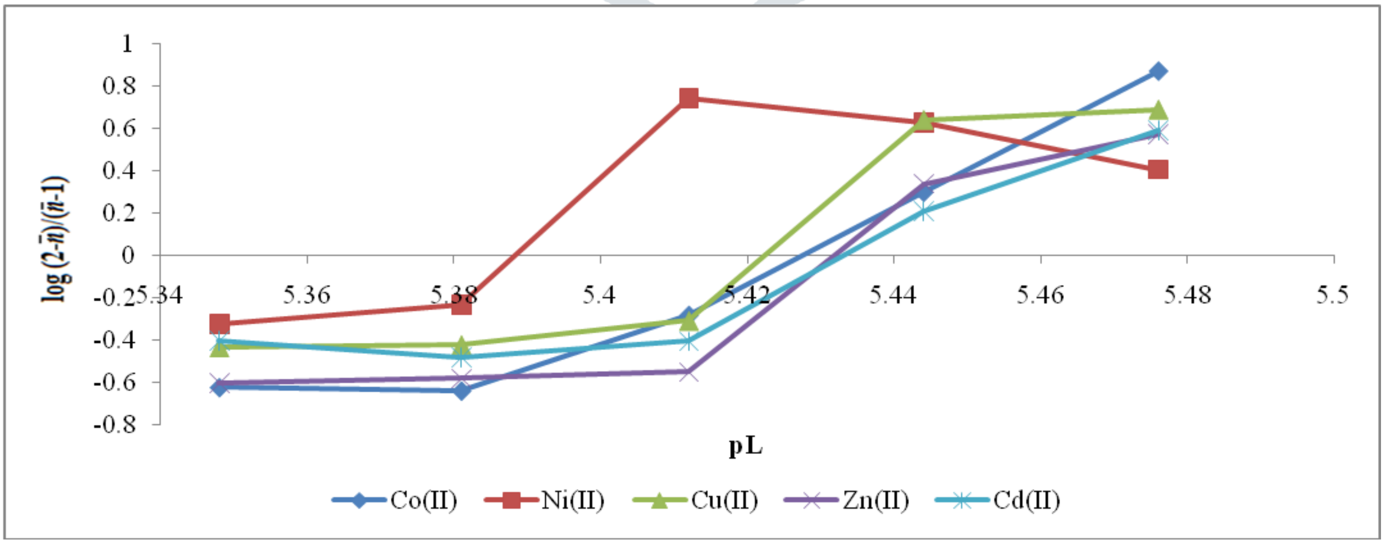


Figure 3.6. Linear plot of log(2- $\bar{n}$) /($\bar{n}$-1) vs pL

IV. CONCLUSION

Potentiometric study of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination compound with valine ligand. The proton-ligand stability constant are calculated by standard expression and compared with previous findings. The order of stability of bivalent metal complexes is found in the order of Cu(II)>Ni(II)>Co(II)>Zn(II)>Cd(II).

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